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THE INSOLUBLE CHROMICYANIDES

By

FREDERICK VAN DYKE CRUSER, A. M.

Dissertation

Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University

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INTRODUCTION.

As comparatively little is known about the chemistry of the insoluble chromicyanides, and as the work that has been done is of an early date, a more thorough and exhaustive investigation on this subject seemed to be of importance.

F. V. D. C.

ACKNOWLEDGMENT.

This investigation was carried out under the direction of Professor Edmund H. Miller, and I take this opportunity to express my sincere thanks for his kindly interest in the work, and for his valuable assistance.

QUANITATIVE CHEMICAL LABORATORY,
HAVEMEYER HALL, COLUMBIA UNIVERSITY,
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THE INSOLUBLE CHROMICYANIDES.

Potassium Chromicyanide.

Böckman* prepared a salt by heating together solutions of potassium hydroxide, chromium hydroxide, with an excess of potassium cyanide. The liquid is colored reddish brown, and will deposit yellow crystals, which are subsequently purified by recrystallization, which crystals have the same form and analogous composition to the potassium salt of ferricyanide and cobalticyanide. The formula is $K_3Cr_2(CN)_{12}$, equivalent to $K_3Cr(CN)_6$ at present. Stridsberg† has worked on the preparation and analysis of potassium chromicyanide. He digests a hot solution of potassium cyanide with potassium chromium chloride for an hour, and evaporates. On cooling the red filtrate, crystals of potassium chromicyanide, $Cr_2CY_3 . 3KCY$ (equivalent to $K_3Cr(Cn)_6$) separate.

Kaiser* prepared the salt by adding to a fairly concentrated solution of potassium cyanide (60 gms.), heated nearly to boiling, small portions at a time of chrom alum (50 gms.). This mixture is heated for about one hour, until its weight is about 300 gms. After cooling, he adds 30 gms. of alcohol (80%), and filters. The filtrate is evaporated, and the yellow crystals which form are filtered off, and purified by recrystallization, until the crystals have a pure yellow color, the first crop of crystals, occluding mother liquor, have a reddish yellow color. The salt is water free, and has the formula $3KCN . Cr_2(CN)_3$, equivalent to $K_3Cr(CN)_6$. The crystal form according to Kopp is the same as that of potassium ferricyanide, namely, monoclinic.

At the ordinary temperature, 100 parts of water dissolve 30.9

*Traite de Chimique Organique, J. Liebig, vol. I., p. 174; Gmelin, Handbook of Chemistry, vol. VII., p. 420; Handwörterbuch d. chem. Fehling, vol. II., p. 663; Jahresb, 1864, vol. 17, p 302.

†Jahresb, 1864, vol. 17, p. 304; N. Arch. ph. nat. XXII., p. 151.

‡Annalen der Chemie und Pharmacie, III. suppl. p. 163; Gmelin Hand 4 aufl. 4, 335; Gmelin Handbook of Chemistry, VII., p. 420; Handwörterbuch d. chem. Fehling, p. 663; Jahresb. 1864, vol. 17, p. 302; Chem. Central. 1865, p. 259.

parts of the salt.* It is insoluble in absolute alcohol, but easily soluble in dilute alcohol. The water solution can be evaporated without decomposition.

Sodium hydroxide, sodium carbonate, ammonium hydroxide, and ammonium carbonate are without effect either in the cold or on boiling. Dilute acids color the solution red, forming violet chromium salts after standing a long time, and evolving prussic acid. By heating this effect is quickly obtained.

The salt dissolves slowly in conc. sulphuric acid, giving a yellow solution, and no change occurs after standing twenty-four hours.

With conc. nitric acid, an orange yellow jelly is formed, which, on being filtered and washed, dissolved only in much water, and this solution did not give the reactions of potassium chromicyanide.

Conc. and dilute hydrochloric acids readily decompose it.

The pulverized salt, which is nearly white in color, becomes intensely yellow when heated to 100° C. On cooling, the color disappears. Ignited, it colors brown, then black, and after continued heating finally forms chromium trioxide. Heated red hot in a stream of hydrogen gas, there remains, besides undecomposed potassium chromicyanide, a black compound, containing chromium, nitrogen and carbon, which is undecomposed by acids and alkalies.

O. T. Christensen† prepared the salt by reducing potassium dichromate by alcohol, in a hydrochloric acid solution, precipitating the chromium as hydroxide, dissolving the same in acetic acid, and treating with potassium cyanide. He obtained 45 grams of salt from 50 grams of potassium dichromate.

In 1903 L. O. Beatty investigated the method of preparation of potassium chromicyanide, and found that the methods of Kaiser, Stridsberg, and Christensen did not give satisfactory results. The method finally adopted by him was a modification of the method of Christensen, which is as follows:

The chromium chloride and potassium chloride obtained by reduction of 50 grams of potassium dichromate with alcohol and hydrochloric acid, after evaporation, was dissolved in 150 c. c.

*Storer, Dictionary of Solubilities, 1864; Comey, Dictionary of Solubilities, 1896. Watts' Dictionary.

†J. für Prac. chem. 1885, 139, 2, 31, p. 163; [2], 23, 52.

of water. This solution was heated, and added slowly to a hot solution of 100 grams of potassium cyanide dissolved in 200 c. c. of water, stirring constantly. The mixture was digested hot for several hours. This was filtered, and evaporated in vacuo to concentration, filtered from the separated chromium hydroxide, and cooled in an ice mixture. The crystals were filtered off, and washed first with dilute (50%), and then with strong alcohol (95%). No alcohol was used for precipitating the salt. The salt was recrystallized as often as necessary to free it from potassium chloride. Contrary to what Kaiser states, he says that the potassium chromicyanide is decomposed by boiling even in a vacuum.

His yield was less than 50%.

Experimental.

In carrying out this work, we are indebted to Mr. L. O. Beatty, who furnished some of the potassium chromicyanide. This salt was purified by recrystallizations over sulphuric acid in a vacuum.

Some potassium chromicyanide was prepared by Beatty's method, but the method finally used, after also testing Christensen's method, was a modification of the former. Sixty grams of chromium trioxide was dissolved in 150 c. c. of conc. hydrochloric acid, and 75 c. c. of water. 75 c. c. of 95% alcohol was added to the mixture, a little at a time, and then the solution was evaporated to dryness. The residue was dissolved in 225 c. c. of boiling water, and added slowly to a hot solution of 150 grams of potassium cyanide dissolved in 300 c. c. of water. The solution was stirred vigorously after each addition of the chromium solution. The mixture was digested for several hours, and then filtered on a Brückner funnel. The filtrate was allowed to evaporate in the air, large crystals of potassium chromicyanide forming, which were very pure, and consequently required only one or two recrystallizations.

During the formation of the salt, the mother-liquor was examined from time to time under the microscope, and in this way great assistance was obtained in finding how well the salt was forming.

If a large excess of potassium cyanide is used, a thick deep

red solution is obtained, from which alcohol will not precipitate potassium chromicyanide; but a syrup is formed at the bottom of the dish.

The salt obtained by recrystallization has a clear yellow color, and, according to M. A. Lamme, of the Department of Mineralogy, the crystal form is orthorhombic, although most generally stated as monoclinic.

The salt heated five hours at 100° C. in a water-jacketed air bath, did not lose in weight. When heated at 102° C. in an air bath for three hours, there was no loss in weight.

Three grams heated to 147° C. lost 0.7 milligram. At this temperature the salt has a deep reddish yellow color.

At 159° C. the salt began to decompose, losing 2.3 milligrams in weight, and the crystals turning dark in spots. The temperature was increased, and at 196° C. the total loss in weight was only 3.2 milligrams. On ignition at a red heat the substance becomes black, and melts, the residue finally having a green color (Cr_2O_3). The crystals decrepitate when strongly heated.

One gram of pure potassium chromicyanide was dissolved in 300 c. c. of water, and the solution allowed to stand in the light for several weeks at the ordinary temperature. The salt slowly decomposes, the solution becoming cloudy.

One gram of the salt heated red hot in a porcelain boat in a glass tube gave no water of crystallization, the weight of the calcium chloride tube remaining practically the same.

0.7026 grams of the salt was analyzed by the following method. It was decomposed by boiling with aqua regia, the solution being boiled down with conc. hydrochloric acid several times to get rid of the excess of nitric acid. The solution was finally diluted with water, and the chromium precipitated three times from the boiling hot solution by ammonium hydroxide in slightest excess. The filtrates were evaporated to dryness, and ignited to drive off the ammonium salts, the residue taken up with water, evaporated again, and ignited. The weight of the impure potassium chloride gave 36.3% of potassium.

The residue was dissolved in hot water, an excess of hydrochlorplatinic acid added, and the solution evaporated. More hydrochlorplatinic acid was added, then alcohol, until about 75% by volume, and the solution allowed to stand over night in a

platinum dish. The potassium chlorplatinate was filtered, washed, dissolved by boiling water into a weighed platinum dish, and after evaporation, weighed. Weighing the potassium as sulphate did not give satisfactory results.

The precipitate of chromium hydroxide was washed into a porcelain casserole, and treated with an excess of sodium peroxide. The solution was boiled for 15-20 minutes, after the addition of more peroxide.

The solution was allowed to cool, and then diluted with water to 500 c.c. volume. This was made acid by 10 c.c. concentrated sulphuric acid in excess, and titrated by a standard solution of ferrous sulphate, (64.052 grams per litre), using a spot test, with a very dilute, freshly prepared solution of potassium ferricyanide. The ferrous sulphate was standardized at the same time by titration against a weighed quantity of potassium chromate, using the above conditions. This was the method used for the determination of chromium throughout the work.

Before this method was decided upon, 0.5207 grams of potassium chromate was dissolved in water, the chromium reduced in a hydrochloric acid solution by alcohol, and precipitated as chromium hydroxide. This was treated as above (sodium peroxide, etc.), and required the same number of c.c. of ferrous sulphate solution as the same weight of potassium chromate, both solutions being titrated under the same conditions.

The addition of an excess of Mohr's salt to the acid chromate solution, and subsequent titration with a standard potassium permanganate solution, did not give accurate results, as the end point was obscured by the green chromium salt formed. When the precipitated chromium hydroxide was ignited and the chromium weighed as sesqui-oxide, the results were slightly high, due to the occlusion of salts by the hydroxide, sulphates especially causing this trouble.

In order to determine the percentage of nitrogen in the salt, 0.5005 gram was decomposed by boiling with 10 grams of potassium sulphate, 1 drop of metallic mercury, and 25 c.c. of concentrated sulphuric acid. The solution was then allowed to cool, water added, then potassium sulphide in excess, and the ammonia, which was liberated by an excess of sodium hydroxide, was distilled into standard $N/_5$ sulphuric acid, and the excess of acid

titrated as usual with sodium hydroxide solution, using cochineal as an indicator. The results of the analyses follow:

		calculated		*found*
3K	117.45	36.05%		36.01%
Cr	52.1	15.99%		16.03%
6C	72.0	22.1 %	by difference	21.97%
6N	84.24	25.86%		25.99%
		100.00		100.00

The formula $K_3Cr(CN)_6$ is therefore confirmed.

The following reagents were used for determining the chemical properties of potassium chromicyanide, and its compounds:

Concentrated hydrochloric acid	sp. gr.	1.20
Concentrated nitric acid	" "	1.42
Concentrated sulphuric acid	" "	1.84
Dilute hydrochloric acid at 24° C	" "	1.0815
Dilute nitric acid at 24° C	" "	1.232
Dilute sulphuric acid at 24° C	" "	1.186
Acetic acid at 24° C	" "	1.017
Ammonium hydroxide strong	" "	0.900
Ammonium " dilute	" "	0.9775

Double normal sodium hydroxide.

Double normal sodium carbonate.

Normal potassium cyanide.

Aqua regia (1 pt. conc. nitric + 3 pts. conc. hydrochloric acid).

Sodium peroxide.

Ammonium sulphide.

Potassium chromicyanide is decomposed by boiling with water and sodium peroxide. The solution, made acid with acetic acid, gave a yellow precipitate with lead acetate.

It is decomposed by concentrated hydrochloric acid, in the cold, more readily on boiling, giving a green solution.

It is decomposed by concentrated nitric acid, giving a green solution on boiling.

It dissolves slowly in concentrated sulphuric acid giving a yellow solution; which, on boiling, decomposes, giving a red, violet, and then a green solution.

It is decomposed by dilute sulphuric, hydrochloric or nitric acids, giving a green solution readily on boiling.

Aqua regia decomposes the salt more readily on heating.

Cadmium Chromicyanide.

According to Kaiser,* cadmium salts give a white precipitate.

Experimental.

One gram of potassium chromicyanide was dissolved in 50 c.c. water, and to this solution was added a solution of cadmium chloride ($CdCl_2 . 2H_2O$), 2 grams dissolved in 50 c.c. of water. A white precipitate with a slight greenish tinge immediately formed. This precipitate was washed thoroughly by decantation, and finally filtered and dried @ 100° C in water-jacketed air bath.

This compound decomposed readily on ignition in a porcelain crucible, giving cadmium oxide and metallic cadmium which deposited on the cover of the crucible. Consequently, this method could not be used for decomposing the compound for analysis.

0.4017 gram of the dried substance was treated with dilute hydrochloric acid, the solution boiled down to low bulk, and the acid treatment repeated in order to get complete decomposition. After most of the acid was evaporated, the solution was diluted to about 500 c.c., and the cadmium precipitated as sulphide by hydrogen sulphide. The cadmium sulphide was filtered and washed, and finally dissolved in dilute hydrochloric acid, evaporated almost to dryness, diluted with water, and neutralized by a sodium hydroxide solution. One gram of potassium cyanide was added, and the solution electrolyzed by 0.17 amp. and 3.75 volts.

The filtrate containing the chromium was evaporated to low bulk, and the chromium precipitated by ammonium hydroxide and ammonium sulphide from a boiling solution. The chromium hydroxide after being washed with boiling water, was washed into a casserole, and treated with sodium peroxide, boiled, treated

*Annalen der Chemie und Pharmacie, III. suppl. p. 170.

with more peroxide, boiled until the peroxide was decomposed, and finally titrated with ferrous sulphate under the previous conditions.

		calculated	*found*
3Cd	337.38	44.73%	41.45%
2Cr	104.2	13.82%	12.76%
12CN	312.48	41.45%	

12.76 : 13.82 : : 41.45 : X

X = 44.89% Cd

The percentages, therefore, give the ratio 3Cd to 2Cr.

One gram of cadmium chloride was dissolved in 50 c.c. of water, and to this solution was added two grams of potassium chromicyanide dissolved in 50 c.c. of water. The precipitate formed was white, with a slight greenish tinge, and was washed, filtered and dried as before. 0.4060 gram was taken, and analyzed as before, with the following results:

Cd	44.73%	41.72%
Cr	13.82%	12.93%

12.93 : 13.82 : : 41.72 : X

X = 44.59% Cd.

The percentages, therefore, give the ratio 3Cd to 2Cr.

The formula given to the compound therefore is $Cd_3Cr_2(CN)_{12}$.

Cadmium chromicyanide is readily soluble in an excess of potassium cyanide, and ammonium hydroxide.

Concentrated hydrochloric acid immediately decomposes it, giving a red solution, which becomes green. This takes place more quickly on boiling. Concentrated nitric acid has the same effect, but action is slower in the cold. Concentrated sulphuric acid acts more slowly than either of the above.

Dilute hydrochloric, nitric and sulphuric acid decompose the compound, giving off hydrocyanic acid, and forming a green solution quickly on boiling, but slowly in the cold. Aqua regia dissolves it quickly. On boiling with sodium peroxide, it is decomposed.

The compound is decomposed by ammonium sulphide, sodium hydroxide and sodium carbonate.

Acetic acid decomposes the compound slowly on boiling.

Cobalt Chromicyanide.

Berzelius* states that colbalt salts give a brown precipitate, which remains brown when dry. As given in Watts' Dictionary,† chromicyanide of cobalt is a blue precipitate. According to Gmelin,‡ salts of protoxide of cobalt yield a blue precipitate with sesqui-cyanide of chromium. Kaiser‡ states that cobalt salts give with potassium chromicyanide, a flesh-colored precipitate insoluble in acids, but soluble in ammonium hydroxide, giving a yellow solution.

Experimental.

One gram of the potassium salt was dissolved in 50 c.c. of water, and to this was added a solution (50 c.c.) of 2 grams of cobalt nitrate ($Co(NO_3)_2 . 6H_2O$). The mixture was stirred thoroughly. A light rose-colored precipitate was formed, which was washed by decantation. After ten washings (400 c.c. water each) the precipitate would not settle, even after standing twenty-four hours. It was filtered, and dried at 100° C in a water-jacketed air-bath. The color of the dried sample was yellowish brown. 0.5227 gram of the substance was ignited in a porcelain crucible, and then fused with sodium peroxide, treated with more sodium peroxide, and then allowed to cool. The fusion was leached out with water, the precipitate filtered, and washed with boiling water. The precipitate was dissolved in hot dilute sulphuric acid, the acid neutralized with ammonium hydroxide, and then 100 c.c. of ammonium hydroxide was added, and three grams of ammonium sulphate. The solution was electrolyzed with a current of 2.5 amperes and 4.75 volts, until a portion gave no color with ammonium sulphide.

The solution containing the chromium was boiled to decompose all the sodium peroxide, and then titrated with ferrous sulphate under the standard conditions.

		calculated	*found*
3Co	177.	29.81%	22.86%
2Cr	104.2	17.55%	13.59%
12CN	312.48	52.63%	

$$13.59 : 17.55 : : 22.86 : X$$

$$X = 29.52\% \text{ Co.}$$

*Berzelius Lehrbuch, 1845, vol. III., p. 1075.
†Watt's Dict. Chem. vol. II., 1872, p. 205.
‡Gmelin Handbook of Chemistry, vol. VII., p. 495.
‡Annalen der Chemie und Pharmacie, III., suppl. p. 170; Handwörterbuch d. chem. Fehling, vol II., p. 663; Jahresb. 1864, vol. 17, p. 302.

Two grams of cobalt nitrate, dissolved in 50 c.c. of water, was precipitated by two grams of potassium chromicyanide dissolved in 50 c.c. water.

The precipitate was light rose in color. Three hundred c.c. of water were added, and after being washed by decantation three times, the precipitate became so colloidal that 8 grams of magnesium chloride were added from time to time, and the washing proceeded with. The precipitate was filtered, and dried as before. 0.3420 gram of the substance was taken and analyzed by the previous method.

	calculated	*found*
Co	29.81%	21.64%
Cr	17.55%	12.65%

$$12.65 : 17.55 : : 21.64 : X$$

$$X = 30.02\% \text{ Co.}$$

The formula $Co_3Cr_2(CN)_{12}$ is therefore given to the compound, being precipitated either by an excess of the cobalt salt or the potassium chromicyanide.

Cobalt chromicyanide is readily soluble in an excess of potassium cyanide. It is decomposed by boiling with sodium peroxide, giving a black precipitate, and a yellow solution of chromate. Also decomposed by ammonium sulphide. Ammonium hydroxide decomposes the compound, but does not entirely dissolve it. Sodium hydroxide decomposes the compound rapidly, sodium carbonate slowly. It is insoluble in cold or boiling acetic acid. Concentrated sulphuric acid, and concentrated hydrochloric acid dissolve it in the cold, very readily on boiling. It is not readily soluble in concentrated nitric acid, even on boiling.

Aqua regia decomposes the compound, but it is not entirely dissolved, even on boiling. It is very slowly soluble in dilute sulphuric, hydrochloric, or nitric acids, being least soluble in the last. On boiling, the dilute sulphuric and hydrochloric acids readily dissolve it, but with nitric acid only slowly.

Cuprous Chromicyanide.

Kaiser* states that by treating cupric chromicyanide with a stream of hydrogen sulphide, or by sulphurous acid, a red com-

*Annalen der Chemie und Pharmacie, III. suppl. p. 166.

pound is formed, which is probably cuprous chromicyanide ($3Cu_2CY \cdot Cr_2CY_3$, equivalent to $Cu_3Cr(CN)_6$ at present).

Experimental.

One gram of potassium chromicyanide was treated with a slight excess of a solution of cuprous chloride, in about 75 c.c. bulk. An orange yellow precipitate immediately formed, which was filtered and washed immediately on a porcelain Gooch crucible. This precipitate was dried at 100° C in a water-jacketed air-bath, and 0.5043 gram taken for analysis. This was dissolved in dilute nitric acid, evaporated to low bulk, water added, and a little ammonium hydroxide, and the solution electrolyzed, using a current of 0.35 ampere and 2.1 volts.

Some chromium was oxidized by the current to chromate. Consequently, after all the copper was deposited, the electrolyte was boiled with alcohol, and then the chromium precipitated as chromium hydroxide, and treated as usual, the solution being titrated with ferrous sulphate under the standard conditions.

		calculated	*found*
3Cu	190.8	47.80%	45.01%
Cr	52.1	13.05%	12.24%
6CN	156.24	39.15%	

$$12.24 : 13.05 : : 45.01 : X$$

$$X = 47.99\% \text{ Cu.}$$

corresponding to the formula $Cu_3Cr(CN)_6$.

Cuprous chromicyanide is readily soluble in an excess of potassium cyanide.

Readily dissolved by concentrated nitric acid in the cold or on boiling. Dilute nitric acid dissolves it, very quickly on boiling. It is readily decomposed by aqua regia, giving a green solution. It is decomposed by concentrated hydrochloric acid, slowly going into solution in the cold, but quickly on boiling. The dilute acid acts similarly.

Cold concentrated sulphuric acid dissolves it slowly, but quickly on boiling. The dilute acid acts similarly, but slower than with the concentrated acid. On boiling with the dilute acid it dissolves quickly, giving a green solution.

Cupric Chromicyanide.

Kaiser* states that in the cold, copper sulphate gives a blue precipitate, containing a little potassium, as shown by his analysis, and which he calculates to copper. By mixing at 75° C a concentrated solution of a copper salt with dilute potassium chromicyanide solution, the precipitate was free from potassium.

From his analysis he gives the formula $3CuCY . Cr_2CY_3$, corresponding to $Cu_3Cr_2(CN)_{12}$ at the present time.

On heating this compound formed in the cold, at 40° C., it loses water irregularly, and if the temperature is raised, it changes from blue to blue-green, green, yellow-green, and finally reddish-gray at 100° C, carrying variable amounts of water. This red salt, on being treated with water will not become blue again. It is insoluble in cold acids, dilute or concentrated, but dissolves on heating. Also insoluble in cold ammonium hydroxide, and sodium hydroxide. On boiling with the latter, dark brown copper oxide is finally precipitated.

Treated with hydrogen sulphide, the compound is reduced to a red substance, which, he says, is probably $3Cu_2CY . Cr_2CY_3$ (equivalent to $Cu_3Cr(CN)_6$ at the present time), copper sulphide not being precipitated. Sulphurous acid gives the same compound.

Comey† gives the formula $Cu_3(Cr(CN)_6)_2$ to the cupric compound, and states that it is a precipitate insoluble in dilute or concentrated acids, except on heating; insoluble in ammonium or potassium hydroxides plus water.

Experimental.

One gram of potassium chromicyanide was dissolved in 50 c.c. of water, and to this was added with constant stirring one and a half grams of copper sulphate ($CuSO_4 . 5H_2O$). A precipitate immediately formed, having a robin's egg blue color. The color changed on standing to green. This compound was washed by decantation, filtered in a Gooch crucible, and dried at 100° C in a water-jacketed air-bath. The color of the dried substance was

*Annalen der Chemie und Pharmacie, III. suppl. p. 166; Handwörterbuch d. chem. Fehling, vol. II., p. 663; Jahresb. 1864, vol. 17, p. 302.

†Dictionary of Solubilities. 1896.

reddish purple. 0.4682 gram was taken for analysis, and dissolved in dilute nitric acid. After boiling for about two hours the solution was electrolyzed. To the filtrate from the electrolysis ammonium hydroxide and ammonium sulphide were added, and the solution boiled. The precipitated chromium hydroxide was filtered, washed and then washed into a casserole, and treated with sodium peroxide as usual. When the peroxide was completely decomposed the solution was cooled and treated with ferrous sulphate under the standard conditions.

		calculated	*found*
3Cu	190.8	31.41%	32.23%
2Cr	104.2	17.15%	17.50%
12CN	312.48	51.44%	

$$17.15 : 17.50 : : X : 32.23$$
$$X = 31.58\% \text{ Cu.}$$

One gram of crystallized copper sulphate was dissolved in 50 c.c. of water, and to this was added a solution of one and a half grams of the potassium chromicyanide dissolved in 50 c.c. of water. A precipitate immediately formed, having the same color as the previous one, but it was so colloidal that in order to wash it by decantation, potassium sulphate and magnesium chloride were used. Volume of water added for each washing was about 400 c.c. This precipitate was filtered, dried and analyzed by the preceding method.

	calculated	*found*
Cu	31.41%	30.96%
Cr	17.15%	16.96%

$$17.15 : 16.96 : : X : 30.96$$
$$X = 31.31\% \text{ Cu.}$$

The formula $Cu_3Cr_2(CN)_{12}$ is therefore given to this compound, being precipitated either by an excess of the copper salt, or vice versa.

Cupric chromicyanide is readily soluble in an excess of potassium cyanide. It is decomposed by an excess of ammonium hydroxide in the cold, giving a blue solution, and a precipitate. Ammonium sulphide gives a black precipitate of copper sulphide. It is decomposed by sodium hydroxide, and by sodium carbonate, the latter giving a blue solution, and a yellowish green precipitate.

It is dissolved by aqua regia; readily by concentrated sulphuric acid in the cold, giving a red solution, which becomes violet, and finally green. Concentrated hydrochloric acid readily dissolves it in the cold, more quickly on boiling. Concentrated nitric acid decomposes it, but only gives a clear green solution on boiling. It is very slowly soluble in cold dilute hydrochloric, nitric, and sulphuric acids, while on boiling the first two readily dissolve it, but the sulphuric dissolves it slowly. It is insoluble in cold acetic acid.

Boiled with sodium peroxide, and water, it is decomposed, giving a green solution. On the addition of acetic acid, a precipitate formed. This was removed by filtration, and then lead acetate gave a yellow precipitate to the filtrate.

Ferrous Chromicyanide.

According to Kaiser,* potassium chromicyanide gives with ferrous solutions, a red, very pulverulent precipitate. If precipitated at 70° C, it is practically potassium free, two analyses averaging 0.25% of potassium. If heated to 100° C, there is a great loss of hydrocyanic acid, and the black mass resulting no longer dissolves by warming with hydrochloric acid, while the compound dried over sulphuric acid readily dissolves in hydrochloric acid. To the substance dried over sulphuric acid he gives the formula $3FeCN \cdot Cr_2(CN)_3 \cdot 20$ aq., corresponding to $Fe_3Cr_2(CN)_{12} \cdot 20$ aq. at the present time, but states that the point at which the compound has not yet lost any water is very difficult to determine accurately, because the substance contains so much water of crystallization. The substance is decomposed by shaking with sodium hydroxide. Liebig† states that potassium chromicyanide gives a brick-red precipitate with ferrous salts. Watts‡ states that the precipitate is brick-red, while Storer‡ gives the formula $3FeCN \cdot Cr_2(CN)_3$ (?) equivalent to $Fe_3Cr_2(CN)_{12}$ at present.

Experimental.

One gram of potassium chromicyanide dissolved in 50 c.c. of

*Annalen der Chemie und Phamacie, III., suppl. p. 169; Handwörterbuch d. chem. Fehling, vol. II., p. 663; Jahresb. 1864, vol. 17, p. 302.

†Traite de Chimique Organique, J. Liebig, vol. I., p. 174.

‡Watts' Dictionary of Chemistry, vol. II., 1872, p. 205.

‡Storer, Dictionary of Solubilities, 1864.

water, was treated with three and a half grams of Mohr's salt, dissolved in 50 c.c. of water, containing two drops of concentrated sulphuric acid. A brick-red granular precipitate immediately formed, which was washed thoroughly by decantation, using water containing a few drops of sulphuric acid.

The precipitate was filtered, and dried at 100° C in a water-jacketed air-bath. The color of the dried substance was dark green. 0.32 gram was ignited in a porcelain crucible for one and a half hours, and then fused with sodium peroxide, allowed to cool, and the fusion leached out with water. After boiling some time the ferric hydroxide was filtered and washed with boiling water, dissolved in hot dilute sulphuric acid (containing 10 c.c. of concentrated acid), the iron reduced by passing the solution through a Jones reductor, and titrated with standard potassium permanganate solution, using the conditions for standardization.

The solution containing the chromium was boiled, and then titrated with ferrous sulphate under the standard conditions.

		calculated	*found*
$3Fe''$	167.7	28.70%	22.12%
$2Cr$	104.2	17.83%	13.85%
$12CN$	312.48	53.47%	

$$13.85 : 17.83 : : 22.12 : X$$
$$X = 28.48\% \text{ Fe.}$$

Two grams of Mohr's salt, dissolved in 100 c.c. of water containing two drops of concentrated sulphuric acid, was treated with two grams of potassium chromicyanide. A brick-red precipitate immediately formed, which was washed as before, and after drying at 100° C., 0.5176 gram was analyzed by the preceding method, with the following results:

		calculated	*found*
$3Fe''$	167.7	28.70%	22.06%
$2Cr$	104.2	17.83%	13.75%
$12CN$	312.48	53.47%	

$$13.75 : 17.83 : : 22.06 : X$$
$$X = 28.60\% \text{ Fe.}$$

From the above results the formula $Fe_3Cr_2(CN)_{12}$, is given to the compound.

Ferrous chromicyanide is decomposed by sodium hydroxide and ammonium hydroxide, giving a brown precipitate, by sodium carbonate giving a green precipitate, and by ammonium sulphide. Potassium cyanide immediately turns the precipitate dark-red, but does not dissolve it. It is decomposed by boiling with sodium peroxide and water.

Aqua regia immediately decomposes the compound, in the cold or on boiling. It is most soluble in hydrochloric acid, concentrated or dilute acid slowly dissolving it in the cold, but very quickly on boiling, giving a green solution.

Dilute or concentrated nitric acid in the cold, decomposes it, giving a precipitate of a dirty yellow color. On boiling with the dilute acid, a clear solution is obtained, but the precipitate does not dissolve on boiling with the concentrated acid, except when diluted with water.

Concentrated sulphuric acid immediately decomposes it, hot or cold.

Cold dilute sulphuric acid acts slower than hydrochloric acid, but on boiling a clear solution is quickly obtained. It is not decomposed by cold acetic acid.

Manganous Chromicyanide.

Kaiser* states that the manganese salt is white, crystalline, and insoluble in dilute acids.

Experimental.

One gram of potassium chromicyanide was dissolved in 50 c.c. of water; one and three-quarters grams of manganese chloride ($MnCl_2 . 4H_2O$) was dissolved in 50 c.c. of water. The second solution was added to the first, stirring constantly. A greenish-white precipitate formed immediately. Under the microscope this precipitate was seen to consist of small crystals, apparently isometric. Four hundred c.c. of water were added, and the compound, after being filtered and washed twelve times with water was dried at 100° C in a water-jacketed air-bath. When dried it had a light brown color. If the compound is dried in a desiccator, in a vacuum, over sulphuric acid, it has a buff color.

*Annalen der Chemie und Pharmacie, III. supplement p. 170; Handwörterterbuch d. chem. Fehling, vol. II., p. 663; Jahresb. 1864, vol. 17, p. 302.

The compound was analyzed by several methods. A portion was ignited in a porcelain crucible, and then fused with sodium peroxide, but this introduced silica and alumina, which had to be subsequently separated, and the results were very poor. Another portion was dissolved in hydrochloric acid, and the chromium precipitated four times by ammonium hydroxide. The manganese could not be separated from the chromium by this method. The filtrates were combined, evaporated to dryness and ignited; taken up with dilute nitric acid and the manganese precipitated by bromine. The manganese dioxide was filtered, and the filtrate evaporated to dryness and ignited. The residue was extracted with water, and gave only a trace of K_2PtCl_6 when precipitated in the usual manner with hydrochlorplatinic acid, and alcohol.

Finally, 0.5504 gram of the compound was dissolved in dilute hydrochloric acid, evaporated to low bulk, more acid added and the solution was again evaporated. Water was added, and then sodium peroxide in excess, the solution being boiled until the peroxide was decomposed. The precipitate was filtered, and washed with boiling water, then dissolved in dilute hydrochloric acid and sulphurous acid. The sulphur dioxide was boiled out of the solution, and the preceding process repeated four times until the manganese was finally free from chromium. The solutions containing the chromium as chromate were boiled to make sure of complete decomposition of the peroxide, and then titrated with ferrous sulphate under the previous conditions.

To the solution containing the manganese, one and a half grams of ammonium phosphate were added, and then ammonium hydroxide until very slightly alkaline, and the solution digested until the manganese phosphate became crystalline. The precipitate was filtered, washed and ignited, being weighed as manganese pyrophosphate.

		calculated	*found*
3Mn	165.18	28.37%	23.06%
2Cr	104.2	17.91%	14.58%
12CN	312.48	53.72%	

$$14.58 : 17.91 :: 23.06 : X$$

$$X = 28.33\% \text{ Mn.}$$

One gram of manganese chloride was dissolved in 50 c.c. of water, and precipitated by two grams of potassium chromicyanide

dissolved in 50 c.c. of water. The precipitate formed was filtered, washed and dried, and analyzed as before. The weight taken for analysis was 0.5590 gram.

	calculated	*found*
Mn	28.37%	23.14%
Cr	17.91%	14.69%

$$14.69 : 17.91 :: 23.14 : X$$
$$X = 28.21\% \text{ Mn.}$$

The compound has, therefore, the formula $Mn_3Cr_2(CN)_{12}$.

The compound is decomposed by sodium peroxide, giving a precipitate of manganese dioxide, and a yellow solution of chromate. Decomposed by boiling with concentrated hydrochloric, nitric, sulphuric acids, and aqua regia, giving a green solution. Readily soluble in an excess of potassium cyanide. Decomposed by an excess of ammonium hydroxide, sodium hydroxide, sodium carbonate and ammonium sulphide. Dissolves very slowly in dilute hydrochloric, nitric or sulphuric acids, but readily on boiling, giving a green solution; only slightly soluble in cold acetic acid, more so on boiling.

Mercurous Compound.

According to Berzelius* mercurous salts give a white precipitate with potassium chromicyanide, which makes the solution at the bottom brown, while the precipitate becomes dark. The color of the liquid soon disappears, and a compound of chromium cyanide with a little mercury remains behind.

Kaiser† states that mercurous nitrate gives a dark gray precipitate with potassium chromicyanide, insoluble in nitric acid and ammonium hydroxide.

Experimental.

0.5 gram of potassium chromicyanide was dissolved in 50 c.c. of water. 2.5 grams of mercurous nitrate was dissolved in 100 c.c. of water and filtered. The latter solution was quickly added to

*Berzelius Lehrbuch, 1845, vol. III., p. 1075.

†Annalen der chemie und Pharmacie, III. suppl. p. 170; Handwörterbuch d. chem. Fehling, vol. II. ,p. 663; Jahresb. 1864, vol. 17, p. 302.

the first. A yellowish white precipitate formed, which quickly darkened, turning finally to gray, and which settled rapidly. The solution did not then smell of hydrocyanic acid. One hundred c.c. of water were added, and the solution stirred. The precipitate settled rapidly, leaving the supernatant liquid reddish-yellow, which rapidly became darker in color. The precipitate darkened, becoming smaller in volume, and on stirring the solution hydrocyanic acid could be readily detected. On standing for a day or so the solution became green, due to the color of the chromium salt. The gray precipitate proved to be nothing but metallic mercury in a very finely-divided state. This was filtered and washed, dissolved in dilute nitric acid, part of the acid neutralized by ammonuim hydroxide, and the solution electrolyzed, using a platinum dish as cathode. The dish was dried in a desiccator over night, after washing the deposited mercury with water. Current used was 0.18 ampere, and voltage 2.3.

Total weight of mercury found was 0.4679 gram.

The reaction takes place probably in the following steps: First, mercurous chromicyanide is precipitated, which then decomposes, giving mercurous cyanide, which then decomposes, giving mercuric cyanide, which slowly dissolves, and metallic mercury.

If the reaction takes place as above stated, 0.5 gram of the potassium salt would precipitate 0.4605 gram of mercury, while 0.4679 gram was found.

Nickel Chromicyanide.

Kaiser* states that solutions of nickel salts give a bluish-green precipitate, very voluminous, becoming green on boiling, insoluble in dilute acids, but soluble in ammonium hydroxide with a grayish-green color.

Experimental.

One gram of potassium chromicyanide was dissolved in 50 c.c. of water. Two grams of nickel nitrate ($Ni(NO_3)_2 . 6H_2O$) was dissolved in 50 c.c. of water, and added to the first solution, stirring constantly. A voluminous light greenish-blue precipitate immediately formed. About 400 c.c. of water were added, and the solution was added to the first, stirring constantly. A greenish- washed by decantation, until the washings gave no color with

*Annalen der Chemie und Pharmacie, III. suppl. p. 170; Handwörterbuch d. chem. Fehling, vol. II., p. 663; Jahresb. 1864, vol. 17, p. 302.

ammonium sulphide. The precipitate was then filtered on a Brückner funnel, and dried in a water-jacketed air-bath at 100° C. The color of the dried compound was black. 0.5 gram of the substance was dissolved by dilute nitric acid, and the separation of the chromium from the nickel attempted by the addition of ammonium hydroxide, in the presence of ammonium chloride, and reprecipitation of the chromium. The results were inaccurate. Then 0.3657 gram was taken and ignited for about two hours in a porcelain crucible, and then allowed to cool. When cold the residue was mixed with sodium peroxide and fused some time. The fusion was leached out with water and filtered. The precipitate was washed with boiling water, and then dissolved in hot dilute sulphuric acid. The solution was evaporated to about 100 c.c. and three grams of ammonium sulphate were added, and 100 c.c. of ammonium hydroxide in excess, and the solution electrolyzed, using 2½ amperes and 3 volts, until 20 c.c. of the solution gave no color with ammonium sulphide.

The filtrate containing the chromium as chromate was boiled to insure the complete decomposition of the peroxide, and then titrated under the previous conditions.

		calculated	*found*
3Ni	176.1	29.71%	24.25%
2Cr	104.2	17.58%	14.37%
12CN	312.48	52.71%	

14.37 : 17.58 : : 24.25 : X

X = 29.67% Ni.

Two grams of nickel nitrate were dissolved in 50 c.c. of water, to which were added two grams of potassium chromicyanide dissolved in 50 c.c. of water. The precipitate resembled the first in color, but was very difficult to wash, as it became colloidal.

The precipitate was washed by decantation, adding eight grams of magnesium chloride from time to time in order to make the precipitate settle. The compound was finally filtered and dried. 0.648 gram of the substance, not quite dry, was analyzed as before, giving the following results:

	calculated	*found*
3Ni	29.71%	18.13%
2Cr	17.58%	10.76%

10.76 : 17.58 : : 18.13 : X

X = 29.62% Ni.

The formula $Ni_3Cr_2(CN)_{12}$ is, therefore, given to the compound, being precipitated either by an excess of nickel salt or of potassium chromicyanide.

The substance is readily soluble in an excess of potassium cyanide, and ammonium hydroxide. It is readily decomposed by ammonium sulphide. It dissolves slowly in the cold in dilute hydrochloric, nitric or sulphuric acids, but readily on boiling, giving a clear green solution.

Slowly soluble in concentrated hydrochloric, nitric, or sulphuric acids, being much more soluble in concentrated sulphuric acid than in the other two. On boiling, all three acids readily dissolve it, forming clear green solutions.

It is slowly decomposed by aqua regia in the cold, quite readily on boiling, giving a green solution after a few minutes.

On boiling with sodium peroxide and water, it is decomposed, but not very readily, precipitating green nickel hydroxide. The filtrate contains sodium chromicyanide. Sodium hydroxide behaves similarly. Sodium carbonate decomposes it slowly in the cold. The compound is insoluble in cold acetic acid, but is slightly soluble on boiling.

Silver Chromicyanide.

Berzelius* states that silver salts give a white precipitate with potassium chromicyanide, which is gray when dry.

Kaiser† states that silver chromicyanide is of a deep yellow color, and in the dry state unaffected by light. It is noted for its stability, being unaffected after twelve hours' treatment with hydrochloric, nitric acid, or ammonium hydroxide. He says that the only solvent is potassium cyanide, and that hydrochloric reprecipitates silver chromicyanide. Dried at 20° to 30° C., it retains its yellow color, while at 100° it has a rose-red color, and loses 0.6% of its weight. He gives the formula $3AgCN \cdot Cr_2CN_3$, equivalent to $Ag_3Cr(CN)_6$ at present, and states that there was some undecomposed substance in the silver chloride, making the percentage of silver high and the chromium low. According to Watts,‡ silver nitrate gives a white precipitate.

*Berzelius Lehrbuch, 1845, vol. III., p. 1075-76.

†Annalen der Chemie und Pharmacie, III., suppl. p. 167; Handwörterbuch d. chemie, Fehling, vol. II., p. 663; Jahresb. 1864, vol. 17, p. 302.

‡Watts' Dictionary of Chemistry, vol. II., 1872, p. 205.

Storer* gives chromicyanide of silver $3AgCN \cdot Cr_2(CN)_3$, equivalent to $Ag_3Cr(CN)_6$ at present, as a precipitate. Comey† says that silver chromicyanide $Ag_3Cr(CN)_6$ is insoluble in all solvents excepting potassium cyanide.

Böckmann‡ states that potassium chromicyanide forms a white precipitate with silver salts, like the composition of the potassium salt. When heated it decomposes into cyanogen gas, metallic silver and chromium cyanide. Hydrogen sulphide passed through the solution containing silver chromicyanide in suspension, gives silver sulphide, and hydrochromicyanide acid.

Experimental.

One gram of potassium chromicyanide was dissolved in 50 c.c. of water and treated with two grams of silver nitrate dissolved in 50 c.c. of water. An orange yellow voluminous precipitate immediately formed, which settled rapidly.

This precipitate was washed by decantation, until the washings gave no test for silver on the addition of sodium chloride. The precipitate was filtered and dried at 100° C in a water-jacketed air-bath, and when dry was of rose-red color.

Difficulty was encountered in the analysis of this compound. The substance was dissolved in concentrated nitric acid, and dilute sulphuric acid, and heated for some time. The silver was precipitated as silver chloride, which gave about 0.7% of silver too high, while about 0.5% of chromium too low. This corresponds quite closely to the results given by Kaiser.‡ Several analyses were made with the same result. It was thought that the difficulty was with incomplete decomposition of the silver compound. Consequently, the following method was finally used, giving good results: 0.5962 gram of the substance was treated with concentrated nitric acid, and dilute sulphuric acid, the solution boiled down to low bulk, more nitric acid added, and the above repeated three times, finally evaporating until nearly all the nitric acid was eliminated. If the solution is evaporated too far an acid sulphate of chromium will be formed, which is then in-

*Dictionary of Solubilities, 1864.

†Dictionary of Solubilities, 1896.

‡Gmelin, Handbook of Chemistry, vol. VIII., p. 31; Traite de Chimique Organique, J. Liebig, vol. 1, p. 174.

‡Kaiser, Annalen der Chemie und Pharmacie, III. suppl. p. 167.

soluble, on the addition of more acid and boiling. The solution was allowed to cool, and then a little dilute hydrochloric acid was added to precipitate the silver; bulk was about 100 c.c. The silver chloride was filtered on a porcelain Gooch crucible, with a piece of filter paper on the bottom, and dried at 110° C, and weighed. The silver chloride was dissolved in three and a quarter grams of potassium cyanide, and the solution electrolyzed.

The filtrate from the silver chloride precipitation was evaporated to about 100 c.c., and the chromium precipitated as hydroxide by boiling with ammonium hydroxide, and ammonium sulphide. This was washed with boiling water and treated with sodium peroxide, and the chromate formed titrated by ferrous sulphate solution under the standard conditions.

		calculated		*found*
$3Ag$		60.85%	from electrolysis	60.84%
			from AgCl	60.89%
Cr	52.1	9.79%		9.69%
$6(CN)$	156.24	29.36%		

The formula $Ag_3Cr(CN)_6$ is, therefore, given to the compound.

Silver chromicyanide is readily soluble in an excess of potassium cyanide, giving a yellow solution. Ammonium sulphide decomposes the compound, precipitating black silver sulphide. It is decomposed by sodium hydroxide solution, and slightly by ammonium hydroxide. It is insoluble in a solution of sodium carbonate, as in hot or cold acetic acid. By boiling with sodium peroxide and water it is decomposed.

A large excess of concentrated hydrochloric acid dissolves the compound, the solution becoming red, then pink, and finally green. On dilution with water silver chloride is precipitated. When treated with small amounts of acid the decomposition is the same, only silver chloride is precipitated. With concentrated nitric acid it slowly dissolves, giving a yellow solution. On boiling it quickly dissolves, giving a green solution.

It is readily soluble in an excess of concentrated sulphuric acid, the solution becoming red, then pink and finally green.

It is decomposed by aqua regia, giving a precipitate of silver chloride. It is very slightly soluble in cold dilute hydrochloric acid, but decomposes on boiling, giving a green solution and a

precipitate of silver chloride. It is slightly soluble in cold dilute nitric acid, but even on boiling is not entirely dissolved. Dilute sulphuric acid does not attack it as readily as dilute nitric acid, being only very slightly soluble in the cold, but much more soluble on boiling.

Zinc Chromicyanide.

According to Berzelius* zinc salts give a white precipitate with potassium chromicyanide, bluish gray when dry.

Kaiser† states that the zinc precipitate is yellowish white in color, pulverulent and easily soluble in ammonium and sodium hydroxides, but only incompletely decomposed by alkali carbonates. It is insoluble in dilute acids, but somewhat concentrated acids color the compound red, and the solution also.

Gmelin‡ says that the zinc compound is white, turning light bluish gray when dry.

Storer‡ says that chromicyanide of zinc is a precipitate.

Watts†† states that a solution of potassium chromicyanide gives a white precipitate with zinc salts.

Experimental.

One gram of potassium chromicyanide, dissolved in 50 c.c. of water, was treated, stirring constantly with two grams of zinc sulphate ($ZnSO_4 + 7H_2O$), dissolved in 50 c.c. of water. 350 c.c. of water were added, the yellowish-white precipitate which formed immediately was allowed to settle, and then the supernatant liquid siphoned off. The precipitate was filtered and washed and dried at 100° C in a water-jacketed air-bath. When dried over sulphuric acid, at the ordinary temperature, the compound has a straw color. About a half gram of the substance was dissolved in sulphuric acid, and the chromium precipitated four times by ammonium hydroxide, dissolving the precipitate each time in considerable excess of hydrochloric acid. From the results obtained it was found that the separation of chromium from zinc was not complete. The zinc was precipitated from the combined

*Berzelius Lehrbuch, 1845, vol. III., p. 1075.

†Annalen der Chemie und Pharmacie, III. suppl. p. 169; Handwörterbuch d. chem. Fehling, vol. II., p. 663; Jahresb. 1864, vol. 17, p. 302.

‡Gmelin Handbook of Chemistry, vol. VII., p. 425.

‡Storer Dictionary of Solubilities, 1864.

††Watts' Dictionary, vol. II., 1872, p. 205.

filtrates after evaporation as zinc ammonium phosphate, and the potassium was precipitated by an excess of hydrochlorplatinic acid and alcohol, in the usual manner, after igniting to drive off the ammonium salts.

Another sample was analyzed as before, with the exception that the zinc was precipitated first as sulphide after taking out the chromium as before. The sulphide of zinc was dissolved in hydrochloric acid, and the zinc precipitated as before. The results again showed incomplete separation of chromium and zinc.

Finally 0.5157 gram of the substance, dried at 100° C., was dissolved in aqua regia, and the solution boiled down to low bulk several times in a casserole after the addition of hydrochloric acid. The solution was finally diluted with water to a volume of about 400 c.c., and neutralized by ammonium hydroxide, and then made fairly acid with acetic acid, and a stream of hydrogen sulphide passed through the solution in the cold for about two hours. The zinc sulphide was filtered and washed with water, containing a few drops of acetic acid and saturated with hydrogen sulphide gas.

The precipitate was dissolved in hydrochloric acid, the solution evaporated to 100 c.c., and two grams of ammonium phosphate were added, then ammonium hydroxide until the solution was neutral. After digesting on a water-bath at 100° C for two hours the crystalline precipitate was filtered and washed with dilute alcohol. The precipitate was dissolved through the paper into a weighed platinum dish and ignited and weighed as zinc pyrophosphate.

The filtrate containing the chromium was evaporated to about 100 c.c. and treated with ammonium hydroxide, and ammonium sulphide. The precipitate, after being washed with boiling water, was washed in a casserole and treated with sodium peroxide, and the chromium titrated with ferrous sulphate under the standard conditions.

		calculated	*found*
3Zn	196.2	32.01%	29.42%
2Cr	104.2	17.00%	15.68%
12CN	312.48	50.99%	

$$15.68 : 17.00 :: 29.42 : X$$

$$X = 31.90\% \text{ Zn.}$$

The filtrate from the chromium precipitation was evaporated to dryness and ignited until all the ammonium salts were driven off. The residue was taken up with water, boiled and filtered. The solution was evaporated with hydrochlorplatinic acid, absolute alcohol added, and the solution allowed to stand over night. The potassium chloroplatinate was filtered, washed and dissolved by boiling water into a weighed platinum dish, giving 0.35% of potassium, which was somewhat impure from a little organic matter from the alcohol.

One gram of crystalline zinc sulphate was dissolved in 50 c.c. of water, and treated with two grams of potassium chromicyanide, dissolved in the same amount of water. A yellowish white precipitate immediately formed, which was dried and treated as before, giving the following results:

		calculated	*found*
3Zn	196.2	32.01%	31.01%
2Cr	104.2	17.00%	16.41%
12CN	312.48	50.99%	

$$16.41 : 17.00 : : 31.01 : X$$
$$X = 32.13\% \text{ Zn.}$$

From the above results the formula $Zn_3Cr_2(CN)_{12}$ is given to the compound.

Zinc chromicyanide is readily soluble in an excess of potassium cyanide, sodium hydroxide, and ammonium hydroxide. It is decomposed by sodium carbonate solution. Ammonium sulphide decomposes the compound, precipitating white zinc sulphide. Boiled with sodium peroxide and water it gave a clear yellow solution, which yields a yellow precipitate of lead chromate on the addition of lead acetate and acetic acid.

With concentrated hydrochloric acid it decomposes slowly, but very quickly on boiling, giving a red, then green solution. It is readily decomposed by boiling with concentrated nitric or sulphuric acid, giving a green solution in each case.

Aqua regia decomposes it quickly, giving a clear red solution, which becomes green.

Dilute hydrochloric acid in the cold easily dissolves the compound, yielding finally a green solution. Dilute sulphuric acid acts more slowly, while dilute nitric acid decomposes it very

slowly. On boiling all three readily yield a green solution. It is very slightly soluble in boiling acetic acid.

Lead Compounds.

Böckmann* states that potassium chromicyanide gives a white precipitate with basic lead acetate, but no precipitate with lead nitrate. Berzelius† says that lead salts give a white precipitate, which becomes blue on drying. Kaiser‡ states that the neutral lead salt is soluble in water. On evaporation, hydrocyanic acid is given off, the solution becomes green and a grayish-white pulverulent substance separates. He says that it is easy to obtain a basic lead chromicyanide by adding to the yellow solution containing the neutral salt, a mixture of lead acetate and ammonium hydroxide. Also that basic salts can be formed from hydrochromicyanic acid. He thinks that quite a few of these basic salts exist, as on adding to the filtrates either lead acetate or ammonium hydroxide, he obtains repeatedly new compounds containing chromium. Also that the precipitates formed are sometimes easily soluble in an excess of lead solutions, or that the filtrates are precipitated by diluting with water. In other cases this did not happen. He analyzed one of the compounds, and from the results obtained concluded that it was a mixture of different basic salts. The compound was easily soluble in nitric acid and sodium hydroxide solution.

Experimental.

Tenth normal solutions of lead nitrate and lead acetate, with a few drops of acetic acid, gave no precipitate with tenth normal potassium chromicyanide solution, either when added in excess, or vice versa.

Kaiser‡ states that mercuric chloride and stannous chloride solutions behave the same as lead. He states that aluminium, chromium, ferric iron, uranium, give no precipitation with potas-

*Liebig's Chimique Organique, vol. I., p. 174.

†Berzelius Lehrbuch, 1845, vol. III., p. 1075-1076; Gmelin, Handbook of Chemistry, vol. VII., p. 428.

‡Annalen der Chemie und Pharmacie, III., suppl. p. 170; Handwörterbuch d. chem., Fehling, vol. II., p. 663; Jahres, 1864, vol. 17, p. 303.

‡Annalen der Chemie und Pharmacie, III., suppl. p. 170; Handwörterbuch d. chem. Fehling, vol. II., p. 663; Jahresb. 1864, vol. 17, p. 303.

sium chromicyanide in the cold, while on heating, the potassium salt is decomposed. According to Böckmann* the salts of ferric iron give no precipitate. Also given by Watts.†

Experimental.

Tenth normal solutions of the following reagents gave no precipitate with $N/_{10}$ potassium chromicyanide, either when added in excess, or vice versa.

Aluminium sulphate.
Barium chloride.
Calcium chloride.
Bismuth nitrate, with enough nitric acid to prevent hydrolysis.
Ferric chloride.
Lithium chloride.
Magnesium sulphate.
Mercuric nitrate, with a few drops of nitric acid added to dissolve the salt.
Mercuric chloride.
Strontium chloride.
Sodium chloride.
Ammonium chloride.
Caesium chloride.
Rubidium chloride.
Chromium chloride.
Arsenic acid.
Cerous sulphate.
Antimony chloride, with enough hydrochloric acid to keep the antimony in solution.
Antimony chloride, with enough tartaric acid to keep the antimony in solution.
Erbium nitrate.
Beryllium nitrate.
Didymium nitrate.
Ammonium molybdate.
Lanthanum nitrate.
Platinum chloride (hydrochlorplatinic acid).
Sodium chloroplatinate.

*Liebig's Chimique Organique, vol. I., p. 174.
‡Watts' Dictionary of Chemistry, vol. II., 1872, p. 205.

Sodium tungstate.

Ammonium vanadate.

Uranium nitrate.

Columbium potassium fluoride (K_2NbOF_5).

Tantalum potassium fluoride, a saturated solution only.

Arsenious acid, a saturated solution only.

Stannous chloride, with enough hydrochloric acid to keep the salt in solution.

Thorium nitrate.

Thallium sulphate.

Yttrium nitrate.

Zirconium nitrate, with a few drops of nitric acid to clear the solution.

A 5% solution of palladium chloride and a solution of auric chloride gave no precipitate when in excess, or vice versa, to a tenth normal solution of potassium chromicyanide.

BIOGRAPHICAL.

Frederick Van Dyke Cruser entered the School of Chemistry, Columbia University, in October, 1899, and graduated in June, 1903, receiving the degree of B. S. in Chemistry. In June, 1903, was appointed Assistant in Quantitative Analysis, Columbia University and pursued graduate work in chemistry and engineering, receiving the degree of A. M. in June, 1905. In September, 1905, was appointed Lecturer in Analytical Chemistry, Columbia University, and pursued graduate work in chemistry for the degree of Ph. D., under the Faculty of Pure Science, at Columbia University.

Publications: With E. H. Miller.

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